

КРАТКИЕ СООБЩЕНИЯ

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STRUCTURES OF TWO HYDRAZONE COMPOUNDS DERIVED FROM 4-METHYLBENZOHYDRAZIDE

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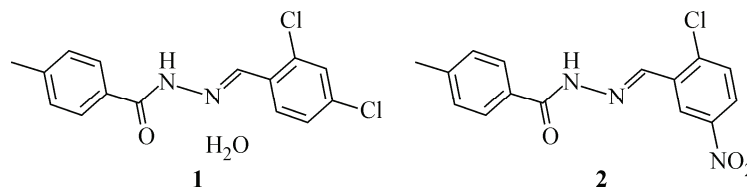
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Two hydrazone compounds *N'*-(2,4-dichlorobenzylidene)-4-methylbenzohydrazide monohydrate (**1**) and 2-chloro-5-nitro-*N'*-(4-methylbenzylidene)benzohydrazide (**2**) derived from 4-methylbenzohydrazide with different benzaldehydes are synthesized and characterized by physicochemical methods and single crystal X-ray diffraction. Compound **1** crystallizes in the orthorhombic space group $P2_12_12_1$ with unit cell parameters $a = 4.714(2) \text{ \AA}$, $b = 13.093(3) \text{ \AA}$, $c = 24.754(3) \text{ \AA}$, $V = 1527.9(8) \text{ \AA}^3$, $Z = 4$, $R_1 = 0.0812$, and $wR_2 = 0.1623$. Compound **2** crystallizes in the monoclinic space group Cc with unit cell parameters $a = 11.564(2) \text{ \AA}$, $b = 13.271(2) \text{ \AA}$, $c = 9.462(2) \text{ \AA}$, $\beta = 96.860(2)^\circ$, $V = 1441.7(4) \text{ \AA}^3$, $Z = 4$, $R_1 = 0.0461$, and $wR_2 = 0.0896$. The crystals of the compounds are stabilized by intermolecular hydrogen bonds as well as $\pi \cdots \pi$ stacking interactions.

Keywords: synthesis, crystal structure, hydrazone compound, hydrogen bonding.

Hydrazides and hydrazones are nowadays of considerable technical and commercial importance due to their wide usage as drugs in medicine and as versatile ligands in coordination chemistry [1–4]. In recent years, a number of hydrazone compounds have been prepared and investigated for their biological properties. In order to carefully study the detailed structures of such compounds, in the present work, two new hydrazone compounds *N'*-(2,4-dichlorobenzylidene)-4-methylbenzohydrazide monohydrate (**1**) and 2-chloro-5-nitro-*N'*-(4-methylbenzylidene)benzohydrazide (**2**) (Scheme 1), derived from 4-methylbenzohydrazide with different aldehydes, were synthesized and structurally characterized.



Scheme 1. The hydrazone compounds

Experimental. Materials and methods. 4-Methylbenzohydrazide, 2,4-dichlorobenzaldehyde, and 2-chloro-5-nitrobenzaldehyde were obtained from TCI. The other chemicals were used as commercially received without further purification. The composition and the structures of the compounds

have been confirmed by means of elemental analysis, ^1H NMR, IR spectroscopy and single crystal X-ray diffraction. Elemental analyses (C, H, and N) were performed on a Carlo Erba instruments CHNS-O EA 1108 automatic equipment. Infrared spectra were recorded using KBr disks on a Shimadzu 8400S FT-IR spectrophotometer. The ^1H NMR spectra were measured on a Varian 200 XL instrument.

Synthesis of 1. A methanolic solution (20 ml) of 4-methylbenzohydrazide (1.5 g, 0.01 mol) was added to a methanolic solution (20 ml) of 2,4-dichlorobenzaldehyde (1.7 g, 0.01 mol). The mixture was refluxed for 2 h, and three quarter of the solvent was evaporated to give yellow precipitate which was filtered off and washed several times with methanol. The yield is 93 %. Yellowish single crystals of the compound were obtained by recrystallization of the compound in methanol. Anal. Calc. (%) for $\text{C}_{15}\text{H}_{14}\text{Cl}_2\text{N}_2\text{O}_2$: C, 55.40; H, 4.34; N, 8.61. Found (%): C, 55.27; H, 4.38; N, 8.55. ^1H NMR: δ 2.33 (s, 3H), 7.41 (d, 2H), 7.92 (d, 2H), 7.96 (d, 1H), 7.40 (d, 1H), 7.71 (s, 1H), 8.97 (s, 1H), 11.03 (s, 1H, NH). IR data (KBr, cm^{-1}): 3427 (br, w, ν_{OH}), 3215 (sh, m, ν_{NH}), 1672 (vs, $\nu_{-\text{C}(\text{O})-\text{NH}-}$), 1627 (vs, $\nu_{\text{C}=\text{N}}$).

Synthesis of 2. Compound **2** was synthesized and crystallized according to the same method as that described for **1**, with 2,4-dichlorobenzaldehyde replaced by 2-chloro-5-nitrobenzaldehyde (1.9 g, 0.01 mol). The yield is 91 %. Anal. Calc. (%) for $\text{C}_{15}\text{H}_{12}\text{ClN}_3\text{O}_3$: C, 56.70; H, 3.81; N, 13.23. Found (%): C, 56.61; H, 3.93; N, 13.10. ^1H NMR: δ 2.33 (s, 3H), 7.41 (d, 2H), 7.77 (d, 1H), 7.92 (d, 2H), 8.26 (d, 1H), 8.49 (s, 1H), 8.97 (s, 1H), 11.22 (s, 1H, NH). IR data (KBr, cm^{-1}): 3213 (sh, m, ν_{NH}), 1671 (vs, $\nu_{-\text{C}(\text{O})-\text{NH}-}$), 1620 (vs, $\nu_{\text{C}=\text{N}}$), 1503 (s, $\nu_{\text{as}} \text{NO}_2$), 1355 (s, $\nu_{\text{s}} \text{NO}_2$).

X-ray diffraction. Single crystals suitable for X-ray diffraction were selected, glued on fiber glasses and successively mounted on a Bruker APEX II CCD diffractometer equipped with graphite-monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). Data collection and reduction were performed using the APEX2 software suite [5]. Empirical absorption corrections were carried out using SADABS [6]. All other calculations were performed using the Bruker SHELXTL package [7, 8]. Anisotropic thermal displacement parameters were refined for all non-hydrogen atoms. The amino H and water H atoms of both compounds were located from difference Fourier maps and refined isotropically, with N—H, O—H, and H \cdots H distances restrained to 0.90(1) Å , 0.85(1) Å , and 1.37(2) Å respectively. The other hydrogen atoms were located in idealized positions. The crystallographic data for the compounds are summarized in Table 1.

Results and discussion. Crystal structure description. The molecular structures of **1** and **2** are shown in Fig. 1, *a* and *b* respectively. Compound **1** contains a hydrazone molecule and a water molecule. Compound **2** contains only a hydrazone molecule, with no solvent molecules reside in. The bond lengths and angles in the compounds are comparable to each other and within normal ranges [9–13]. The water molecules in **1** are linked to the hydrazone molecules through intermolecular O—H \cdots O hydrogen bonds. In the benzohydrazide molecules, the C(9)—N(2) bond lengths are 1.276(8) Å in **1** and 1.273(4) Å in **2**, indicating them as typical double bonds. The distances between C(8) and N(1) atoms (1.356(8) Å for **1**, and 1.370(4) Å for **2**) are intermediate between single and double bonds, due to the conjugation effects of the hydrazone molecules. In the benzohydrazide molecules, the dihedral angles between the C(2)—C(7) and C(10)—C(15) benzene rings are 5.3(5) $^\circ$ for **1** and 1.0(3) $^\circ$ for **2**.

In the crystal structure of **1**, the benzohydrazide molecules are linked by water molecules through intermolecular O—H \cdots O and N—H \cdots O hydrogen bonds to form 1D chains running along the *b* axis (Fig. 2). In the crystal structure of **2**, the benzohydrazide molecules are linked through intermolecular N—H \cdots O hydrogen bonds to form 1D chains running along the *c* axis (Fig. 3). In addition, there are $\pi\cdots\pi$ stacking interactions among the adjacent benzene rings C(2)—C(7) and C(10)—C(15) in compound **2**, with the distances between the ring centroids of 3.715(2) Å and 3.616(2) Å [14].

IR spectra. The broad and weak absorption band at about 3430 cm^{-1} is attributed to the O—H vibrations of the water molecule. The sharp and middle bands at about 3215 cm^{-1} are assigned to the N—H vibrations. The characteristic bands at about 1672 cm^{-1} are assigned to the vibration of the —C(O)—NH— groups, and the other characteristic bands at about 1625 cm^{-1} are attributed to the

Table 1

Crystallographic data for the compounds

| | 1 | 2 |
|--|---|---|
| Empirical formula | C ₁₅ H ₁₄ Cl ₂ N ₂ O ₂ | C ₁₅ H ₁₂ ClN ₃ O ₃ |
| Formula weight | 325.2 | 317.7 |
| Crystal system | Orthorhombic | Monoclinic |
| Space group | <i>P</i> 2 ₁ 2 ₁ | <i>C</i> <i>c</i> |
| Unit cell parameters <i>a</i> , <i>b</i> , <i>c</i> , Å; β, deg. <i>V</i> , Å ³ | 4.714(2), 13.093(3), 24.754(3); 90 | 11.564(2), 13.271(2), 9.462(2); 96.860(2) |
| <i>Z</i> , calculated density | 4 | 4 |
| Absorption coefficient | 0.430 | 0.281 |
| <i>F</i> (000) | 672 | 656 |
| Crystal size | 0.18×0.17×0.15 | 0.15×0.13×0.12 |
| Theta range for data collection | 2.92 – 26.99 | 2.35 – 26.99 |
| Limiting indices | −5 ≤ <i>h</i> ≤ 5, −16 ≤ <i>k</i> ≤ 16, −31 ≤ <i>l</i> ≤ 27 | −14 ≤ <i>h</i> ≤ 14, −15 ≤ <i>k</i> ≤ 16, −11 ≤ <i>l</i> ≤ 11 |
| Reflections collected / unique | 3254 / 1920 [<i>R</i> _{int} = 0.0804] | 2999 / 2218 [<i>R</i> _{int} = 0.0298] |
| Data / restraints / parameters | 3254 / 200 / 4 | 2999 / 203 / 3 |
| Goodness-of-fit on <i>F</i> ² | 1.141 | 1.036 |
| Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] | 0.0812 | 0.0460 |
| <i>R</i> indices (all data) | 0.1906 | 0.0896 |
| Largest diff. peak and hole | 0.308, −0.383 | 0.157, −0.187 |

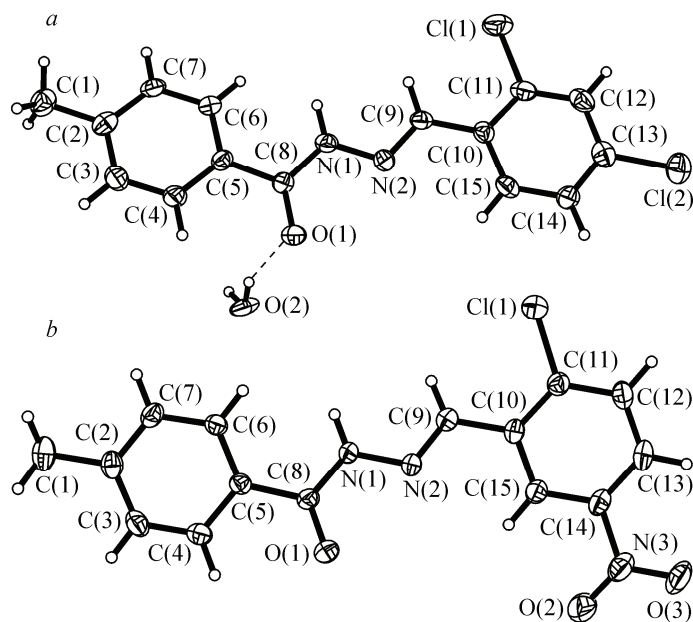


Fig. 1. View of the molecular structure of 1 (a), 2 (b), showing the atom labeling scheme. Displacement ellipsoids are drawn at the 30 % probability level for non-H atoms. Hydrogen bonds are indicated as dashed lines

—C=N— stretching vibrations. The presence of $\nu_{\text{as}}(\text{ONO})$ and $\nu_{\text{s}}(\text{ONO})$ absorption bands at 1502 cm^{-1} and 1353 cm^{-1} respectively in the IR spectrum of 2 suggests the existence of the nitro group.

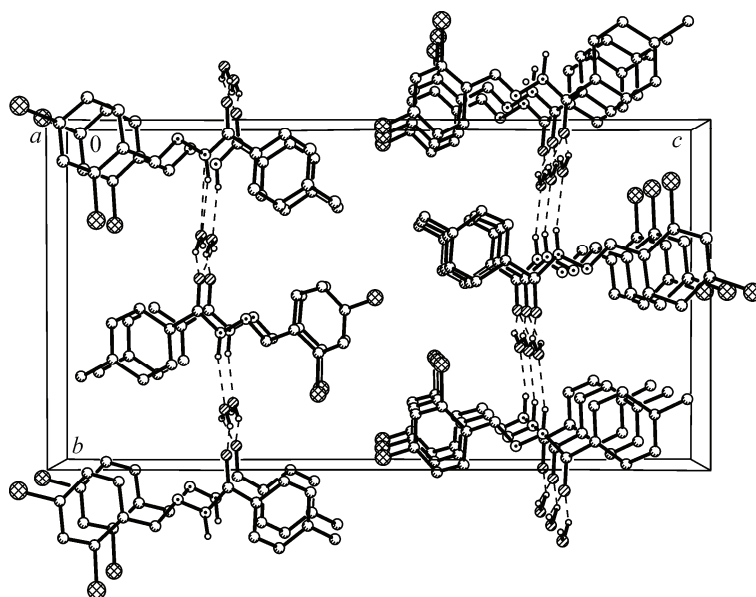


Fig. 2. View of the 1D hydrogen-bond packing diagram along the *b* axis for **1**. Hydrogen bonds are indicated as dashed lines [O(2)—H(2B) = 0.85(1) Å, H(2B)⋯O(1) = 2.02(3) Å, O(2)⋯O(1) = 2.809(8) Å, O(2)—H(2B)⋯O(1) = 155(7)°; O(2)—H(2A) = 0.85(1) Å, H(2A)⋯O(1) = 2.07(3) Å, O(2)⋯O(1) = 2.868(7) Å, O(2)—H(2A)⋯O(1) = 157(8)°; N(1)—H(1) = 0.90(1) Å, H(1)⋯O(2) = 2.08(3) Å, N(1)⋯O(2) = 2.949(6) Å, N(1)—H(1)⋯O(2) = 161(7)°]

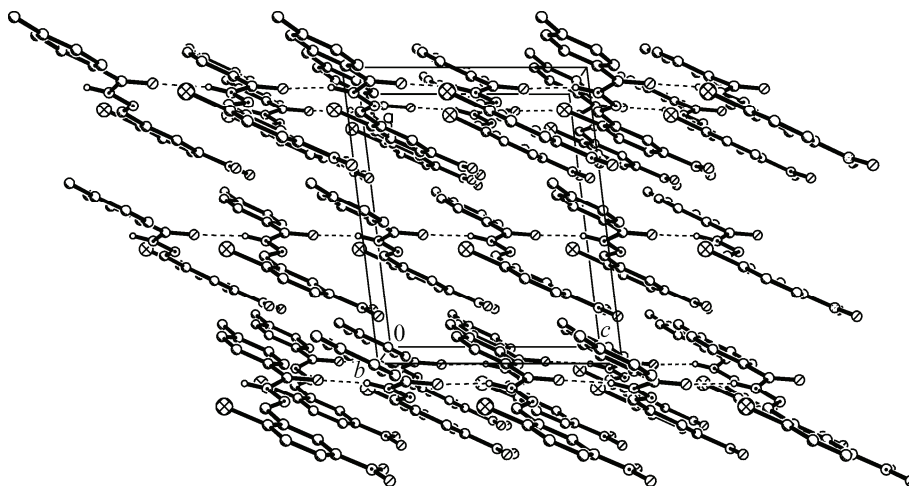


Fig. 3. View of the 1D hydrogen-bond packing diagram along the *c* axis for **2**. Hydrogen bonds are indicated as dashed lines [N(1)—H(1) = 0.90(1) Å, H(1)⋯O(1) = 2.30(2) Å, N(1)⋯O(1) = 3.134(3) Å, N(1)—H(1)⋯O(1) = 153(3)°]

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Supplementary material. CCDC- 821979 for **1** and 821980 for **2** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/const/retrieving.html> or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033 or e-mail: data_request@ccdc.cam.ac.uk.

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